961015 DE
EP-A-0 454 ...

(21) (A1) 2,038,332
(22) 1991/03/15
(43) 1991/09/18
(52) 402-296
C.R. CL. 134-3.3

(51) INTL.CL. [5] C08F-002/10; C08F-022/02; C08F-02?/20; C11D-...

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Preparation of Homopolymers and Copolymers of Monoethylenically Unsaturated Dicarboxylic Acids and Use Thereof

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(30) (DE) P 40 08 696.8 1990/03/17

(57) 5 Claims

Notice: The specification contained herein as filed

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Abstract of the Disclosure: Homopolymers and copolymers of monoethylenically unsaturated dicarboxylic acids of K 7 - 50 which are useful as additives in textile and dishwashing detergent compositions in amounts of from 0.1 to 15% by weight are obtained by free radical polymerization of

(a) monoethylenically unsaturated dicarboxylic acids,
(b) hydroxy-C_2-C_4-alkyl (meth)acrylates and optionally
(c) other water-soluble monoethylenically unsaturated monomers

at a degree of neutralization of the acid group-containing monomers during the polymerization of from 52 to 70%, and contain not more than 1.5% by weight of unpolymerized dicarboxylic acid.

Preparation of homopolymers and copolymers of monoethylenically unsaturated dicarboxylic acids and use thereof

EP-B-0,075,820 discloses a process for preparing copolymers of monoethylenically unsaturated mono- and dicarboxylic acids wherein monomer mixtures of from 10 to 60% by weight of a monoethylenically unsaturated dicarboxylic acid, such as maleic acid, and from 90 to 40% by weight of a monoethylenically unsaturated monocarboxylic acid of from 3 to 10 carbon atoms, such as acrylic acid, are polymerized in an aqueous medium at 60 - 150°C and at a degree of neutralization of from 20 to 80% during the polymerization reaction using from 0.5 to 5% by weight of a water-soluble initiator, based on the monomers. This process gives copolymers containing less than 1.5% by weight of residual, unpolymerized dicarboxylic acid.

DE-A-35 12 223 discloses the preparation of homopolymers and copolymers of maleic acid by copolymerization of maleic acid in an aqueous medium with or without other water-soluble ethylenically unsaturated monomers in the presence of polymerization initiators. In this process, maleic acid is first neutralized with an alkali metal hydroxide or ammonia in a molar ratio of from 100 : 0 to 100 : 90 and then polymerized by the addition of a polymerization initiator. Further alkali metal hydroxide or ammonia is added to the reaction mixture in the course of the polymerization, so that the molar ratio of maleic acid to base is from 100 : 100 to 100 : 130. The polymerization is then completed. According to the examples, however, the ratio of maleic acid to sodium hydroxide solution after the polymerization has ended is not more than 1:1. The polymers thus preparable have a narrow molecular weight distribution and molecular weights within the range from 200 to 20,000. According to said patent application, it is impossible to achieve a high rate of polymerization outside the neutralization range specified for maleic acid. The copolymers are used

for example as scale inhibitors for boiler or desalination systems, as detergent builders and as dispersants for inorganic pigments.

EP-A-0,337,694 concerns a process for preparing maleic acid polymers in the acid form having a number average molecular weight of from 300 to 5,000 and a narrow molecular weight distribution (ratio of M_w : M_n less than 2.5) by polymerizing maleic acid in an aqueous medium, optionally together with from 50 to 0.1% by weight of other water-soluble ethylenically unsaturated monomers, in the presence of metal ions (eg. iron, vanadium and copper ions) in amounts of from 0.5 to 500 ppm and hydrogen peroxide in amounts of from 8 to 100 g/mole of monomer. The polymers thus obtainable are used as water treatment agents. It is true that according to the comparative examples even an up to 50% or 23.7% neutralized maleic acid polymerizes in the presence of an initiator system of hydrogen peroxide and iron ions, but the polymers obtained contain high residual levels of maleic acid.

It is an object of the present invention to provide a process for preparing homopolymers and copolymers of monoethylenically unsaturated dicarboxylic acids which converts a monoethylenically unsaturated dicarboxylic acid content of at least 65% by weight into a polymer containing not more than 1.5% by weight of residual monoethylenically unsaturated dicarboxylic acid monomer.

We have found that this object is achieved according to the present invention by a process for preparing a homopolymer or copolymer of a monoethylenically unsaturated dicarboxylic acid having a K value of from 7 to 50 (determined after H. Fikentscher on the sodium salt of the polymer at pH 7 and 25°C in 1% strength aqueous solution) by free radical polymerization of

(a) a monoethylenically unsaturated C_4-C_6-dicarboxylic

acid,

(b) a hydroxy-C_2-C_4-alkyl acrylate or methacrylate and

(c) another water-soluble monoethylenically unsaturated monomer

in a weight ratio of (a) : (b) : (c) of (100 - 65) : (0 - 35) : (0 - 35) in partially neutralized form in aqueous solution, which comprises setting the degree of neutralization of the acid group-containing monomer(s) to 52-70% during the polymerization, which in the case of the preparation of a copolymer of (a) with an acid group-containing monomer (c), when the degree of neutralization of monomer (a) at the start may be as high as 85%, is achieved by using the acid group-containing monomer (c) in nonneutralized form.

The monomers of group (a) are monoethylenically unsaturated C_4-C_6-dicarboxylic acids. Suitable dicarboxylic acids are for example maleic acid, fumaric acid, itaconic acid, mesaconic acid, methylenemalonic acid and citraconic acid. It is of course also possible to use dicarboxylic anhydrides which on dissolving in water convert into the acid form. Suitable anhydrides of this kind are for example maleic anhydride, itaconic anhydride and methylenemalonic anhydride. Preferred monomers of this group are maleic acid, fumaric acid and itaconic acid, especially maleic acid or the anhydride thereof. The monomers of group (a) are either homopolymerized or copolymerized with one another or with monomers of groups (b) and/or (c). In the case of copolymers, they contain at least 65% by weight, preferably from 80 to 95% by weight, of monomers of group (a) as copolymerized units.

The monomers of group (b) are hydroxy-C_2-C_4-alkyl acrylates and/or methacrylates. Compounds of this type are for example 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl methacrylate, 2-hydroxybutyl acrylate, 2-hydroxybutyl methacrylate, 4-hydroxybutyl acrylate, 4-hydroxybutyl

methacrylate and mixtures thereof, which also includes all isomers and isomer mixtures. Preferred monomers of this group are hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylates and hydroxypropyl methacrylates. The monomers of group (a) are copolymerized with the monomers of group (b) in a weight ratio of (100 - 65) : (0 - 35), preferably (99 - 80) : (1 - 20).

Monomers of group (c) are other water-soluble monoethylenically unsaturated monomers which are copolymerizable with monomers (a) and (b). Examples of monomers of group (c) are C_3-C_{10}-monocarboxylic acids, such as acrylic acid, methacrylic acid, dimethylacrylic acid, ethylacrylic acid, allylacetic acid and vinylacetic acid. Preference is given to using from this group of monomers acrylic acid, methacrylic acid and mixtures thereof. Other suitable monomers (c) are sulfo-containing monomers, eg. vinylsulfonic acid, allylsulfonic acid, methallylsulfonic acid, styrenesulfonic acid, 3-sulfopropyl acrylate, 3-sulfopropyl methacrylate and acrylamidomethylpropanesulfonic acid, and also phosphono-containing monomers, eg. vinylphosphonic acid, allylphosphonic acid and acrylamidomethylpropanephosphonic acid. It is also possible to use acid group-free water-soluble monoethylenically unsaturated monomers as monomers of group (c) in the copolymerization, for example amides such as acrylamide, methacrylamide, N-alkylacrylamides having from 1 to 18 carbon atoms in the alkyl group, eg. N-methylacrylamide, N-dimethylacrylamide, N-tert-butylacrylamide and N-octadecylacrylamide, N-vinylpyrrolidone, N-vinylcaprolactam, N-vinylimidazole, 1-vinyl-2-methylimidazole, 1-vinylimidazoline, 1-vinyl-2-methylvinylimidazoline, N-vinylformamide, N-vinyl-N-methylformamide, N-vinylacetamide, N-vinyl-2-methylacetamide and mixtures thereof. The monomers of group (c) are copolymerized with the monomers of group (a) either alone or together with the monomers of group (b). The weight ratio of (a) : (b) : (c) in the copolymerization is (100 - 65) : (0 - 35) :

(0 - 35). If monomers of group (c) are used in the copolymerization, the amount based on 100 parts by weight of copolymer is preferably from 1 to 20 parts by weight. Preferred monomers of this group are acrylic acid, methacrylic acid and acrylamidomethylpropanesulfonic acid.

To modify the copolymers, it is possible to include monomers of group (d) in amounts of up to 5% by weight, based on the total amount of monomers used in the polymerization. The monomers of group (d) are cross-linkers, for example N,N-methylenebisacrylamide, esters of acrylic acid, methacrylic acid and maleic acid with polyhydric alcohols and polyalkylene glycols, these esters having at least two monoethylenically unsaturated double bonds, eg. glycol diacrylate, glycol dimethacrylate, glycerol triacrylate, glycerol trimethacrylate, polyethylene glycol diacrylates derived from polyalkylene glycols of molecular weight 36 - ca. 2,000, and also the corresponding polyethylene glycol dimethacrylates, polyethylene glycol dimaleates of polyethylene glycols of molecular weights of up to 2,000, glycol dimaleate and also doubly acrylated or methacrylated polyols, such as pentaerythritol and glucose. It is also possible to use crosslinked divinylbenzene, divinyldioxane, pentaerythritol diallyl ether and pentaallylsucrose. If cross-linkers are included in the copolymerization, they are preferably used in an amount of from 0.05 to 5% by weight, based on the total amount of monomers used in the polymerization.

To prepare polymers having a particularly low K value, the monomers are polymerized in the presence of regulators. Suitable regulators are for example mercapto compounds, such as mercaptoethanol, mercaptopropanol, mercaptobutanol, mercaptoacetic acid, mercaptopropionic acid, butylmercaptan and dodecylmercaptan. Other suitable regulators are allyl compounds such as allyl alcohol, hydroxylamine, formic acid, ethylene glycol, propylene

glycol, polyethylene glycol and polypropylene glycol having molecular weights of up to 6,000 and secondary alcohols, such as isopropanol and sec.-butanol. If the polymerization is carried out in the presence of regulators, they are used in an amount of from 0.05 to 20% by weight. It is of course also possible to carry out the polymerization in the presence of both regulators and monomers of group (d), the crosslinkers.

The monomers are subjected to a polymerization initiated with a free radical initiator. Suitable initiators for the polymerization are consequently all compounds which form free radicals under the polymerization conditions, such as azo compounds and peroxides. This also includes redox systems. Preference is given to water-soluble initiators such as persulfates, eg. sodium persulfate, potassium persulfate and ammonium persulfate, and hydrogen peroxide. Especially in those cases where the polymerization is carried out at relatively low temperatures it is advantageous to use redox initiators to speed up the reaction. Such redox initiator systems comprise customary free radical compounds, such as peroxides, persulfates or percarboxylic acids, together with a reducing compound, such as sodium hydrogen sulfite, sodium disulfite, sodium dithionite, sodium formaldehyde sulfoxylate, sulfur dioxide, ascorbic acid or mixtures thereof. It is also possible to use heavy metals, such as iron, copper, nickel, chromium, manganese and vanadium ions, in the form of soluble salts as redox component. The heavy metal ions are added in amounts of from 0.1 to 100, preferably from 0.1 to 10, ppm. It is advantageous in some instances to use not only reducing agents but also heavy metal ions. If reducing agents are present in the catalyst system, their amount is from 0.1 to 10, preferably from 0.2 to 5, % by weight, based on the monomers. The polymerization initiators are used in amounts of from 0.5 to 20, preferably from 2 to 13, % by weight, based on the monomers. If the homopolymers or

copolymers are to have a relatively high maleic acid content, the amount of initiator used will be toward the top end of the above-described range, while copolymers which are to contain from 65 to about 80% by weight of maleic acid as copolymerized units are prepared using initiator quantities within the range from 0.5 to 12% by weight.

The polymerization is carried out with aqueous solutions of the monomers. The concentrations of the monomers in the aqueous solution is customarily from 10 to 70, preferably from 20 to 60, % by weight. The monomers are customarily polymerized within the temperature range from 70 to 150°C, preferably from 80 to 130°C. Particular preference is given to polymerizing under boiling conditions of the reaction mixture. If the polymerization temperature is above the boiling point of the reaction mixture, an appropriately designed pressure apparatus is used. The polymerization can of course also be carried out under reduced pressure. However, it is most simply carried out at atmospheric pressure. As is customary with polymerizations, the polymerization is carried out with the exclusion of oxygen, for example in an inert gas atmosphere, eg. under nitrogen. During the polymerization it is advantageous to ensure thorough mixing of the reactants. This can be achieved for example in any reactor which is equipped with a stirrer, for example a horseshoe stirrer.

According to the present invention, the degree of neutralization of the acid group-containing monomers is adjusted to 52 - 70% during the homopolymerization or copolymerization, so that the polymers obtained after the polymerization has ended are already partially neutralized in that the acid group-containing monomers present as copolymerized units have been neutralized to 52 - 70%, preferably 55 - 65%.

In preparing copolymers by copolymerizing monomers (a) with acid group-containing comonomers (c) it is

initially possible to set a degree of neutralization of monomers (a) which is above the range from 52 to 70% if the acid group-containing monomers (c) are subsequently added to the initially charged monomers (a), being up to 85% neutralized, in nonneutralized form. After all the monomer (c) has been added this then too produces a partially neutralized copolymer having a degree of neutralization in respect of the copolymerized acid groups of from 52 to 70%, preferably from 55 to 65%. If copolymers are to be prepared from monomers (a) and (b) or from (a) and acid group-free monomer (c) and optionally monomer (d) or from monomers (a) and (b), acid group-free monomers (c) and optionally monomers (d), it is preferable first to introduce the monomers of group (a) in the form of a 10-70% strength aqueous solution having a degree of neutralization of from 52 to 70%, preferably from 55 to 65%, and then to add the comonomers and the initiator to the reaction mixture at a rate commensurate with the rate of copolymerization; that is, to add the comonomers and the initiator to the reaction mixture at such a rate that the polymerization reaction remains readily controllable, so that the heat of polymerization can be safely removed.

Another way of maintaining the degree of neutralization within the abovementioned range during the copolymerization of monomers (a) with acid group-containing monomers (c) and optionally (b) and (d) is to neutralize the monomers (a) in aqueous solution to 52 - 70% and to add the acid group-containing monomers (c) and optionally the other comonomers to the initially introduced aqueous solution of the partially neutralized monomers (a) together with a base, so that the acid group-containing monomers (c) likewise have a degree of neutralization within the range from 52 to 70%, preferably from 55 to 65%. However, the acid group-containing monomers (c) may also be added to the initially introduced aqueous, partially neutralized solution of monomer (a) in an

already partially neutralized form with a degree of neutralization which is within the specified range. And the acid group-containing monomer (c) may also be added to an at least 60% neutralized monomer (a), with the lower degree of neutralization of 52%. The only requirement is that the acid group-containing units (c) and (a) present in the copolymer have a total degree of neutralization of from 52 to 70%. But in some instances it may also be advantageous to add the acid group-containing monomers (c) in a partially or completely neutralized form, in which case, however, the initially introduced monomers (a) must then be neutralized to a correspondingly smaller percentage.

The neutralizing agent used is an alkali metal base, ammonia or an amine. Preference is given to using sodium hydroxide and potassium hydroxide. Suitable amines for use as neutralizing agents are for example ethanolamine, diethanolamine, triethanolamine, morpholine and mixtures thereof.

To prepare colorless or only slightly colored homopolymers and copolymers from monomers (a) to (d), the polymerization is advantageously carried out in the presence of water-soluble phosphorus compounds in which the phosphorus has an oxidation number of from 1 to 4, the water-soluble alkali metal or ammonium salts thereof, water-soluble $PO(OH)_2$-containing compounds and/or water-soluble salts thereof. Preference is given to using phosphorous acid. The contemplated phosphorus compounds are used for reducing the discoloration of polymers in amounts of from 0.01 to 5% by weight, based on the monomers used. The contemplated phosphorus compounds are described in connection with other polymerization processes in EP-A-0,175,317.

The process according to the present invention gives polymers having K values of from 7 to 50, preferably from 8 to 30 (measured at 25°C on 1% strength aqueous solutions of the polymers adjusted to pH 7 with

sodium hydroxide solution). The homopolymers and copolymers obtainable by the process according to the present invention contain relatively low levels of residual monomers of group (a). The residual monomer level of maleic acid is for example not more than 1.5%, based on solids. The polymers thus obtainable can therefore be directly used for the intended purposes or after complete neutralization. The homopolymers and copolymers are usable for example as additives in fabric and dishwashing detergent compositions in amounts of from 0.1 to 15% by weight, in either case based on the formulation as a whole.

Dishwashing compositions contain for example from 5 to 20% by weight of an ammonium or alkali metal carbonate or of an ammonium or alkali metal sulfate, at least 2% by weight of an alkali metal silicate and from 0.5 to 8% by weight of a low-foam surfactant and also, as a further essential component, a polymer obtainable by the process according to the present invention. They may contain up to 94% by weight of sodium silicate and up to about 50% by weight of an ammonium or alkali metal carbonate or sulfate. They may also contain compounds which give off active chlorine, for example the potassium or sodium salts of dichloroisocyanurate, in which case the active chlorine content of the formulation may be up to 3% by weight. In addition, gluconic acid or glucoheptonic acid and the alkali metal salts thereof may be present in amounts of up to 20% by weight. Dishwashing detergent compositions may contain still other customary additives, for example antifoams, dyes, scents, dustproofing agents and commercial polymers, for example polyacrylates or copolymers of 70% by weight of acrylic acid and 30% by weight of maleic acid, in the customary concentrations. Since the compositions of dishwashing agents vary widely, the above statements are to be treated as merely illustrative.

The homopolymers and copolymers obtainable by the

process according to the present invention can also be used in textile washing detergent compositions, hereinafter simply called detergents. In many cases it is necessary for this purpose that the polymer solutions obtained in the polymerization can be dried to a powder or granules in customary dryers such as drum dryers, spray dryers or combined spray/fluidized bed dryers.

The polymers act as incrustation inhibitors and pigment soil dispersants in the detergents. They can be used not only in liquid but also in pulverulent detergents and cleaners. Compared with the copolymers of monomers (a) and acid group-containing monomers disclosed in EP-B-0 025 551, they show in particular improved compatibility in liquid detergent formulations.

The compositions of detergent formulations can vary widely. The same is true of the compositions of cleaner formulations. Detergent and cleaner formulations customarily contain surfactants with or without builders. This applies not only to liquid but also to pulverulent detergent and cleaner formulations. Examples of compositions of detergent formulations customary in Europe, the USA and Japan are found in table form for example in Chemical and Engn. News 67 (1989), 35, and in Ullmanns Encyklopädie der technischen Chemie, Verlag Chemie, Weinheim 1983, 4th edition, pages 63-160.

The above-described polymers are used according to the present invention in detergents which contain up to 45% by weight of phosphate, although the use of the polymers in detergents having a reduced phosphate content (to be understood as meaning a phosphate content of less than 25% by weight of sodium triphosphate) or in phosphate-free detergents and also in cleaners is preferred. The polymers may be added to the detergent formulation in the form of granules, as a paste, as a highly viscous mass, as a dispersion or as a solution in a solvent. The polymers can also be adsorbed at the surface of colorless diluents, for example sodium sulfate, or builders (zeo-

lites or bentonites) and also other solid ingredients of the detergent formulation.

Detergent formulations and cleaner formulations are pulverulent or liquid. They may vary in composition by region and according to the specific intended use.

Universal household detergents for drum type washing machines of the type widely used in Europe usually contain from 5 to 10% by weight of anionic surfactants, from 1 to 5% by weight of nonionic surfactants, from 1 to 5% by weight of foam regulators, such as silicone oils or soaps, from 0 to 40% by weight of a water softener, such as sodium carbonate or pentasodium triphosphate, which may be replaced in whole or in part by the compounds according to the present invention, from 0 to 30% by weight of an ion exchanger such as zeolite A, from 2 to 7% by weight of sodium silicate as corrosion inhibitors, from 10 to 30% by weight of bleaching agents, such as sodium perborate, sodium percarbonate, organic peracids or salts thereof, from 0 to 5% by weight of bleach activators, such as tetraacetylethylenediamine, pentaacetylglucose, hexaacetylsorbitol or acyloxybenzenesulfonate, stabilizers, such as magnesium silicate or ethylenediaminetetraacetate, grayness inhibitors, such as carboxymethylcellulose, methylalkylcellulose and hydroxyalkylcellulose, polyglycols grafted with vinyl acetate, oligomeric and polymeric terephthalic acid/ethylene glycol/polyethylene glycol esters, enzymes, fluorescent whitening agents, scents, fabric softeners, dyes, and diluents.

By contrast, the heavy duty detergents which are widely used in the USA, Japan and neighboring countries in tub type washing machines are usually free of bleaching agents, but on the other hand their anionics content is two or three times higher and they contain more wash alkalis, such as sodium carbonate and sodium silicates (in general up to 25% by weight), but they usually also lack the bleach activators and stabilizers. The levels of

surfactants and other ingredients can be appreciably higher in the case of detergent concentrates, which are available with little or no diluent. Detergents for easy-care and colored fabrics, wool detergents and manual wash detergents likewise usually contain no bleaching agents and low levels of alkaline ingredients together with an appropriately increased surfactant content.

Detergents for the commercial sector are designed for the special conditions of industrial washing (soft water, continuous washing) which make it possible to customize the detergent to the type of article being washed and to the nature of the soil. Combinations are therefore used in which one ingredient predominates or others are completely absent only to be added separately when required. For this reason the surfactants, builders, alkalis and bleaching agents of these detergents vary within wide limits.

Suitable anionic surfactants for the aforementioned pulverulent detergents, or washing powders, are for example sodium alkylbenzenesulfonates, fatty alcohol sulfates and fatty alcohol polyglycol ether sulfates. Individual compounds of this type are for example C_8-C_{12}-alkylbenzenesulfonates, C_{12}-C_{16}-alkanesulfonates, C_{12}-C_{16}-alkylsulfates, C_{12}-C_{16}-alkylsulfosuccinates and sulfated ethoxylated C_{12}-C_{16}-alkanols. Other suitable anionic surfactants are sulfated fatty acid alkanolamines, α-sulfo fatty acid esters, fatty acid monoglycerides or reaction products of from 1 to 4 mol of ethylene oxide with primary or secondary fatty alcohols or alkylphenols. Further suitable anionic surfactants are fatty acid esters and fatty acid amides of hydroxy- or amino-carboxylic or -sulfonic acids, for example the fatty acid sarcosides, glycolates, lactates, taurides or isethionates. The anionic surfactants can be present in the form of the sodium, potassium and ammonium salts and also as soluble salts of organic bases, such as mono-, di- or triethanolamine or other substituted amines. The group of

anionic surfactants also includes the ordinary soaps, ie. the alkali metal salts of natural fatty acids.

Suitable nonionic surfactants (nonionics) are for example addition products of from 3 to 40, preferably from 4 to 20, mol of ethylene oxide with 1 mol of fatty alcohol, alkylphenol, fatty acid, fatty amine, fatty acid amide or alkanesulfonamide. The abovementioned addition products of ethylene oxide may additionally contain up to 90% by weight of propylene oxide as copolymerized unit, based on the polymerized ethylene oxide and propylene oxide. The addition products which contain ethylene oxide and propylene oxide may be modified by incorporation of butylene oxide in amounts of up to 60% by weight, based on the total alkylene oxide content. Of particular importance are the addition products of 5 to 16 mol of ethylene oxide with coco or tallow fatty alcohols, with oleyl alcohol or with synthetic alcohols of from 8 to 18, preferably from 12 to 18, carbon atoms, and also with mono- or dialkylphenols having from 6 to 14 carbon atoms in the alkyl moieties. Besides these water-soluble nonionics, however, it is also possible to use water-insoluble or incompletely water-soluble polyglycol ethers having from 1 to 4 ethylene glycol ether moieties in the molecule, in particular if they are used together with water-soluble nonionic or anionic surfactants.

Further usable nonionic surfactants are the water-soluble addition products of ethylene oxide with polypropylene glycol ethers, alkylenediaminopolypropylene glycol and alkylpolypropylene glycols having from 1 to 10 carbon atoms in the alkyl chain which contain from 20 to 250 ethylene glycol ether groups and from 10 to 100 propylene glycol ether groups, the polypropylene glycol ether chain acting as the hydrophobic moiety.

It is also possible to use nonionic surfactants of the type of the amine oxides or sulfoxides.

The foaming power of the surfactants can be increased or reduced by combining suitable surfactant

types. A reduction can also be achieved by adding non-surfactantlike organic substances.

Further possible formulation ingredients of detergents include monomeric, oligomeric and polymeric phosphonates, ether sulfonates based on unsaturated fatty alcohols, eg. oleyl alcohol ethoxylate butyl ether, and alkali metal salts thereof. These substances can be characterized for example with the aid of the formula $RO(CH_2CH_2O)_n-C_4H_8-SO_3Na$, where n is from 5 to 40 and R is oleyl.

The above-described polymers may also be used as additives in liquid detergents. Liquid detergents contain liquid surfactants or else solid surfactants which are soluble or at least dispersible in the detergent formulation. Suitable surfactants for this purpose are those products which are also used in pulverulent detergents, and also liquid polyalkylene oxides or polyalkoxylated compounds. If the polymers are not directly miscible with the other constituents of the liquid detergent, it is possible to prepare homogeneous mixtures with the aid of a small amount of a solubilizer, for example water or a water-miscible organic solvent, eg. isopropanol, methanol, ethanol, glycol, diethylene glycol or triethylene glycol or corresponding propylene glycols. The amount of surfactant in liquid detergents is within the range from 4 to 50% by weight, based on the formulation as a whole, since in liquid detergents too the proportions of the ingredients vary within wide limits according to regional market conditions or the intended use.

Liquid detergents may contain water in amounts of from 10 to 60, preferably from 20 to 50, % by weight. But they can also be free of water.

Water-free liquid detergents may also contain peroxo compounds for bleaching in suspended or dispersed form. Examples of suitable peroxo compounds are: sodium perborate, peroxocarboxylic acids and polymers having some peroxo-containing groups. Liquid detergents may also

contain hydrotropes. These are compounds such as 1,2-propanediol, cumenesulfonate and toluenesulfonate. If such compounds are used for modifying a liquid detergent, their amount is from 2 to 5% by weight, based on the total weight of the liquid detergent. In many cases an addition of complexing agents has also proved advantageous for modifying pulverulent and liquid detergents. Complexing agents are for example ethylenediaminetetraacetic acid, nitrilotriacetate and isoserinediacetic acid and also phosphonates, such as aminotrismethylenephosphonic acid, hydroxyethanediphosphonic acid, ethylenediaminetetraethylenephosphonic acid and salts thereof. Complexing agents are used in amounts of from 0 to 10% by weight, based on the detergent. Detergents may also contain citrates, di- or triethanolamine, clouding agents, optical brighteners, enzymes, perfume oils and dyes. These substances, if they are used for modifying a liquid detergent, together account for up to 5% by weight. Detergents are preferably phosphate-free. However, they may also contain phosphates, eg. pentasodium triphosphate and/or tetrapotassium pyrophosphate. If phosphates are used, they account for up to 45, preferably up to 25, % by weight of the total formulation of detergent.

The polymers can also combine with other known detergent additives (for example grayness inhibitors, clay dispersants, substances which enhance primary detergency, color transfer inhibitors, bleach activators) in pulverulent and liquid detergents (phosphate-containing and phosphate-free) to create synergistic effects boosting not only the grayness inhibition but also the action of the other detergent additive.

The K values were determined by the method of H. Fikentscher, Cellulosechemie 13 (1932), 58 - 64, 71 - 74; $K=k\times10^3$. The measurements were carried out on 1% strength aqueous solutions of the sodium salts of the polymers at 25°C and pH 7. The residual levels of mono-

meric maleic acid in the polymers were determined polarographically. The percentages of residual maleic acid in the polymer are expressed in terms of solids. The percentages are by weight.

EXAMPLES 1 TO 4 AND COMPARATIVE EXAMPLE 1

A heatable reactor which is equipped with a stirrer, a reflux condenser, a thermometer, an addition means and a nitrogen inlet is charged with 300 g of water, 380.17 g of maleic anhydride, 3 g of 50% strength aqueous phosphorous acid, 20 ml of a 0.035% strength aqueous solution of ammonium iron(II) sulfate and the amount of sodium hydroxide mentioned in Table 1, and this initial charge is heated to the boil under nitrogen. The boiling solution, which is being stirred continuously, is admixed in the course of 5 hours with a solution of 50 g of hydroxypropyl acrylate in 80 g of water and separately therefrom in the course of 6 hours with 266 g of 30% strength hydrogen peroxide. The polymerization is carried out at the boiling point of the reaction mixture. After all the hydrogen peroxide has been added, the reaction mixture is heated at the boil for a further 2 hours. It is then neutralized to pH 6.8 by adding the amounts of 50% strength aqueous sodium hydroxide solution indicated in Table 1. Table 1 also indicates the solids contents of the polymer solutions, the K values of the polymers and the levels of unpolymerized maleic acid in the copolymers.

TABLE 1

Example No.	NaOH quantity [g]	Degree of neutralization [%]	NaOH 50% strength for neutralizing the polymer solution [amount in g]	Solids content [%]	K value	Residual maleic acid [%]
1	170.70	55	115	45.4	12.0	0.56
2	186.20	60	90	45.6	11.6	0.28
3	201.70	65	75	44.3	10.5	0.71
4	217.24	70	56	45.4	10.2	1.48
Comparative Example 1	155.17	50	139	43.8	11.1	2.29

EXAMPLES 5 TO 10 AND COMPARATIVE EXAMPLES 2 TO 4

The reactor described in Example 1 is charged in each case with 300 g of water, 338 g of maleic anhydride and the amount of sodium peroxide mentioned in Table 2, and the contents are heated to the boil. The boiling mixture is admixed in the course of 5 hours with a solution of 100 g of acrylic acid in 110 g of water and separately therefrom in the course of 6 hours with a solution of 20 g of sodium persulfate in 70 g of water and a solution of 56.6 g of 30% strength hydrogen peroxide in 23.34 g of water at a uniform rate, and the polymerization is carried out at the boiling point of the reaction mixture. After all the initiator has been added, the reaction mixture is heated at the boil for a furtheer 2 hours. This produces clear, yellowish polymer solutions whose solids contents are indicated in Table 2. Table 2 also indicates the K values of the polymers and the

residual levels of maleic acid.

TABLE 2

Example No.	Amount of NaOH added to initial charge [g]	Degree of neutralization [%] of initial charge	Degree of neutralization [%] on completed addition	Solids content [%]	K value	Residual maleic acid [%]
5	231.77	84	69.9	53.3	17.2	1.00
6	221.74	80	66.6	52.8	19.1	0.47
7	213.84	77.5	64.5	52.9	20.0	0.16
8	206.94	75.0	62.4	52.6	18.7	0.35
9	193.14	70	58.2	52.6	20.8	0.55
10	179.35	65	54.2	52.5	20.4	1.43
Comparative Example No.						
2	248.33	90	74.9	53.7	15.7	1.87
3	165.55	60	49.5	52.1	20.0	4.09
4	137.96	50	41.6	49.8	15.0	11.30

EXAMPLE 11

The reactor specified in Example 1 is charged with 270 g of water, 401.3 g of maleic anhydride and 213.42 g of sodium hydroxide, and this initial charge is heated to the boil. Immediately the mixture begins to boil it is admixed in the course of 5 hours with a solution of 25 g of acrylic acid in 80 g of water and in the course of 5 hours with a solution of 50 g of sodium persulfate in 120 g of water and separately therefrom with 100 g of 50% strength hydrogen peroxide at uniform rates, and polymerized at the boiling point. After the

initiator has been added, the reaction mixture is heated at the boil for a further 2 hours and then neutralized with 100 g of 50% strength aqueous sodium hydroxide solution. The degree of neutralization of the initial charge was about 65%. After all the acrylic acid had been added, the total degree of neutralization of the carboxylic acid groups in the copolymer was 52.5%. The resulting clear brownish solution had a solids content of 53.4%. The copolymer had a K value of 12.1 and contained 0.12% of monomeric maleic acid.

EXAMPLE 12

The reactor described in Example 1 is charged with 300 g of water, 389 g of maleic anhydride, 7 ml of a 0.1% strength aqueous solution of ammonium iron(II) sulfate and 190.15 g of sodium hydroxide, and this initial charge is heated to the boil. Immediately the mixture begins to boil, it is admixed in the course of 5 hours with a solution of 50 g of acrylic acid, 95.35 g of 58% strength aqueous solution of the sodium salt of acrylamidomethylpropanesulfonic acid and 30.6 g of water and in the course of 6 hours from the start of boiling with a solution of 40 g of sodium persulfate in 120 g of water and 133.33 g of 30% strength hydrogen peroxide at uniform rates. After all the initiator has been added, the reaction mixture is heated at the boil for a further hour and then neutralized with 50% strength aqueous sodium hydroxide solution to pH 7.0. The slightly cloudy brown solution thus obtainable has a solids content of 50.8%. The copolymer has a K value of 13.3 and contains 1.06% of monomeric maleic acid.

EXAMPLE 13

Application testing of the polymers as dishwashing formulation additives

The following pulverulent dishwashing formulation was used to test an example according to the present invention against comparative examples:

32 parts of sodium sulfate

55 parts of sodium metasilicate (anhydrous)
5 parts of sodium carbonate (anhydrous)
3 parts of the addition product of 2 mol of ethylene oxide and 4 mol of propylene oxide with 1 mol of a C_{13}/C_{15} fatty alcohol
5 parts of polymer

The formulation was in each case obtained by mixing the abovementioned products. The polymer product tested is specified below in the Table. To test each individual formulation, 2 g of the formulation were used per liter of tapwater (18° German hardness), and the aqueous solution of the formulation was heated to 80°C. Then sets of flatware were immersed, the solution was stirred with a magnetic stirrer for 5 minutes, and the flatware was left to stand in the aqueous dishwasher liquor at 80°C for a further 5 minutes. Then the flatware was dried unrinsed at 23°C and the film left, if any, was rated on a scale from 1 to 5, where 1 denotes a very poor result, ie. a clearly visible white film, while 5 denotes a very good result, ie. no film at all. The polymers used in the individual formulations and the results are indicated in Table 3.

TABLE 3.

Example	Comparative Example	Polymer (in dishwashing formulation)	K value	Rating of result of using the polymer in dishwashing formulation
-	5	Polyacrylic acid, Na salt	20	1.5 - 2
-	6	Polyacrylic acid, Na salt	40	1.5
-	7	Copolymer of 70% by weight of acrylic acid and 30% by weight of maleic acid	60	1.5 - 2
13	-	Copolymer of Example 2	11.6	4.5

EXAMPLE 14

Testing of polymers as detergent additives

The comparison is against a commercial copolymer of 70% by weight of acrylic acid and 30% by weight of maleic acid in the form of the sodium salt of K 60. This copolymer will hereinafter be referred to as comparative polymer 1.

The performance characteristics tested are the incrustation-inhibiting effect and the soil-dispersing effect (clay dispersion test).

Incrustation inhibitor effect

To test the incrustation-inhibiting effect of the polymers described, each polymer was incorporated into a phosphate-free washing powder. This detergent formulation was used to wash test fabrics made of cotton. The number of wash cycles used was 10. After each cycle the fabric was ironed dry. Following this number of washes the ash content of each test fabric was determined by ashing the fabric. The greater the effectiveness of the polymer in the detergent, the lower the ash content of the test fabric.

Experimental conditions for determining incrustation:

Apparatus:	Launder-O-Meter from Atlas, Chicago
Number of wash cycles:	10
Wash liquor:	250 g, water used containing 4 mmol of hardness per liter (molar ratio of calcium to magnesium = 3 : 1)
Washing time:	30 min at 60°C (including heating up time)
Detergent dosage:	8 g/l
Cotton fabric:	20 g

Detergent (phosphate-free)

12.5% of dodecylbenzenesulfonate (50%)

4.7% of a C_{13}/C_{15} oxo process alcohol polyglycol ether containing 7 ethylene oxide units

2.8% of soap

25% of zeolite A

12% of sodium carbonate

4% of sodium disilicate

1% of magnesium silicate

20% of sodium perborate

5% of copolymer of operative or comparative example (calculated as 100% strength)

0.6% of sodium carboxymethylcellulose

Remainder to 100%: sodium sulfate

Effectiveness of polymers in respect of incrustation inhibition

Copolymer added to detergent formulation	Ash content (%)
No polymer added	1.29
Comparative polymer 1	0.57
Polymer of Example 3	0.59
Polymer of Example 9	0.49

Clay dispersion

The removal of particulate soil from fabric surfaces is augmented by the presence of polyelectrolytes. These polyelectrolytes have the important task of stabilizing the dispersion which forms on detachment of the particles from the fabric surface. The stabilizing effect of anionic dispersants is due to the fact that the adsorption of dispersant molecules at the particle surface increases their surface charge and the repulsion energy. Further factors having a bearing on the stability of the dispersion include steric effects, the temperature, the pH and the electrolyte concentration.

The clay dispersion (CD) test described hereinafter provides a simple means for testing the dispersing power of various polyelectrolytes.

CD test

The model employed to represent particulate soil is finely ground china clay SPS 151. 1 g of clay is thoroughly dispersed in 98 ml of water in the presence of 1 ml of a 0.1% strength sodium salt solution of the polyelectrolyte in a graduated cylinder (100 ml) for 10 minutes. Immediately after stirring, a 2.5 ml sample is taken from the center of the graduated cylinder and diluted with water to 25 ml to measure the cloudiness of the dispersion with a turbidimeter. Further samples were taken after the dispersion had stood for 30 and 60 minutes and assessed turbidimetrically. The cloudiness of the dispersion is reported in NTUs (nephelometric turbidity units). The slower the rate of settling of the dispersion during storage, the higher the measured turbidity values and the stabler the dispersion.

The second physical variable determined is the dispersion constant τ, which describes the time course of the sedimentation process. Since the sedimentation process can be described to an approximation with a monoexponential time law, τ indicates the time within which the turbidity drops to 1/e-th of the original state at time t = 0.

The higher τ, the slower the rate of sedimentation of the dispersion.

Clay dispersion test

Substance tested	Cloudiness in NTUs after storage			Dispersion constant τ
	at once	30 min.	60 min.	
Without polymer	600	37	33	41.4
Comparative polymer 1	640	470	380	97.2
Polymer of Example 3	660	550	500	234.3
Polymer of Example 9	600	540	500	261.0

The superiority of the copolymers according to the present invention over a commercial copolymer having a lower maleic acid content is evident. While the incrustation inhibition effects are approximately the same, the copolymer according to the present invention is distinctly more effective in the clay dispersion test, a measure of primary detergency.

We claim:

1. A process for preparing a homopolymer or copolymer of a monoethylenically unsaturated dicarboxylic acid having a K value of from 7 to 50 (determined after H. Fikentscher on the sodium salt of the polymer at pH 7 and 25°C in 1% strength aqueous solution) by free radical polymerization of

(a) a monoethylenically unsaturated C_4-C_6-dicarboxylic acid,

(b) a hydroxy-C_2-C_4-alkyl acrylate or methacrylate and

(c) another water-soluble monoethylenically unsaturated monomer

in a weight ratio of (a) : (b) : (c) of (100 - 65) : (0 - 35) : (0 - 35) in partially neutralized form in aqueous solution, the degree of neutralization of the acid group-containing monomer(s) being set to 52-70% during the polymerization, which in the case of the preparation of a copolymer of (a) with an acid group-containing monomer (c), when the degree of neutralization of monomer (a) at the start may be as high as 85%, is achieved by using the acid group-containing monomer (c) in nonneutralized form.

2. A process as claimed in claim 1, wherein a copolymer is prepared from monomers (a) and (b) in a weight ratio of (a) : (b) of (99 - 65) : (1 - 35) at a degree of neutralization of monomer (a) of from 55 to 65%.

3. A process as claimed in claim 1, wherein a copolymer is prepared from monomers (a) and (c) in a weight ratio of (a) : (c) of (99 - 65) : (1 - 35) by introducing the monomer (a) into the polymerization reactor, neutralizing it up to 85% with an alkali metal base, ammonia or an amine and then adding an initiator and the acid group-containing monomer (c) in nonneutralized form at a rate commensurate with the rate of polymerization.

4. A process as claimed in claim 1, wherein a copolymer is prepared from monomers (a), (b) and (c) in

a weight ratio of (a) : (b) : (c) of (99 - 65) : (1 - 35) : (1 - 35) at a total degree of neutralization of the acid group-containing monomers of from 55 to 65%.

5. A textile or dishwashing detergent composition containing from 0.1 to 15% by weight, based on the formulation as a whole, of a homopolymer or copolymer of a monoethylenically unsaturated dicarboxylic acid having a K value of from 7 to 50 (determined after H. Fikentscher on the sodium salt of the polymer at pH 7 and 25°C in 1% strength aqueous solution), obtainable by free radical polymerization of

(a) a monoethylenically unsaturated C_4-C_6-dicarboxylic acid,

(b) a hydroxy-C_2-C_4-alkyl acrylate or methacrylate and

(c) another water-soluble monoethylenically unsaturated monomer

in a weight ratio of (a) : (b) : (c) of (100 - 65) : (0 - 35) : (0 - 35) in aqueous solution, with a degree of neutralization of the acid group-containing monomer(s) of 22-70% during the polymerization, which in the case of the preparation of a copolymer of (a) with an acid group-containing monomer (c), when the degree of neutralization of monomer (a) at the start may be as high as 85%, is achieved by using the acid group-containing monomer (c) in nonneutralized form.